

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION

INTERNATIONAL APPLICATION PUBLISHING CENTER



WO 9603970A1

(51) International Patent Classification 6 :

A61K 7/06, 47/00

(43) International Publication Date: 15 February 1996 (15.02.96)

(21) International Application Number: PCT/US95/09960

(22) International Filing Date: 7 August 1995 (07.08.95)

(30) Priority Data:
08/286,544 5 August 1994 (05.08.94) US

(71) Applicant: WITCO CORPORATION [US/US]; One American Lane, Greenwich, CT 06831-2559 (US).

(72) Inventors: MANNING, Monna, Marie; 654 Wilson Avenue, Columbus, OH 43205 (US). ALLARDICE, Andrea, Susan; 4778 Hayden Boulevard, Columbus, OH 43221 (US). FRIEDLI, Floyd; 9406 Avemore Court, Dublin, OH 43107 (US).

(74) Agents: BLACK, Donald, T. et al.; Scully, Scott, Murphy & Presser, 400 Garden City Plaza, Garden City, NY 11530 (US).

(81) Designated States: AU, BR, CA, CN, JP, KR, MX, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published

With international search report.

(54) Title: BIODEGRADABLE QUATERNARY HAIR AND SKIN CONDITIONERS

(57) Abstract

Disclosed are conditioning compositions for the hair and skin containing compounds of the formula $(R^1)(R^2)N(CHCH_2OC(O)R)_2X^-$; wherein R^1 is alkyl containing 1 to 6 carbon atoms, or hydroxyalkyl containing 1 to 6 carbon atoms; R^2 is alkyl containing 1 to 6 carbon atoms, or benzyl; X^- is an anion; and R is alkyl and alkylene of 12 to 22 carbon atoms having 0 to 3 carbon-carbon double bonds, provided that at least 2 different chain lengths R are present and 0, 1 and 2 such double bonds are present.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LJ	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

1 BIODEGRADABLE QUATERNARY HAIR AND SKIN CONDITIONERS

BACKGROUND OF THE INVENTION

5 The present invention relates to conditioning hair and skin, particularly the hair and skin of the human body. More particularly, the present invention relates to methods of imparting conditioning to the hair and skin and to compositions useful as hair conditioners and skin conditioners.

10 Hair conditioning imparts to the hair many attributes which are perceivable and are considered to be desirable. That is, hair conditioners are used so that the hair feels, to the touch, smoother and softer. In addition, hair conditioners are used to render the 15 hair more easily rinsable when it is washed or rinsed, to improve the wet and dry combability of the hair, and to impart to the hair greater ease of detangling and greater manageability to combing, brushing and styling.

Skin conditioners are used generally to 20 improve the feel of the skin to the touch, rendering the skin softer and smoother feeling. In addition, skin conditioners are used to impart to the skin a feeling of fullness and smoothness as well as freedom from dryness and freedom from roughness.

25 Numerous compositions have been available commercially for conditioning the hair and the skin. More recently, however, governmental regulations and the preferences of the individual consumer have given rise to concerns that consumer products including hair 30 conditioners and skin conditioners not pose excessive risks of damage to the environment. While these

-2-

1 concerns have generally been addressed by improvements
in composition so that materials when discarded or
washed away are relatively less damaging to the
environment, it would be useful to be able to formulate
5 hair conditioning products and skin conditioning
products which are in fact biodegradable. In this way,
the desirable conditioning properties would be provided,
and the product upon disposal or removal by washing and
the like would be capable of biodegrading, that is,
10 being converted by the processes normally encountered in
waste water treatment and the like into components which
pose an even lesser risk of harm to the environment and
which can be dealt with ever more easily by the
customary processes for treating solid waste and waste
15 water.

Unfortunately, actual experience prior to the
present invention has generally found that agents that
might be considered in hair conditioning compositions
and skin conditioning compositions, which agents are
20 found to be biodegradable, perform only poorly if at all
as conditioning agents for the hair and skin. In fact,
this experience has been encountered so uniformly that
there has seemed to be essentially a negative
correlation between biodegradability and effectiveness
25 as a conditioner for the hair and skin; that is, an
agent found to be biodegradable would accordingly not be
expected to, and would not, perform adequately as a
conditioning agent for the hair and skin.

Thus, there remains a need for conditioning
30 agents and for compositions containing such agents
exhibiting biodegradability and also exhibiting

-3-

1 exemplary performance as conditioners for the hair and skin. The present invention satisfies this need, even in the face of expectations to the contrary as drawn from experience with many biodegradable compounds.

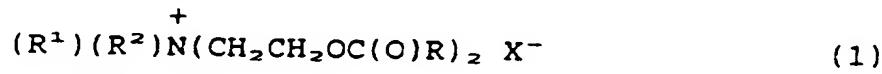
5

BRIEF SUMMARY OF THE INVENTION

One aspect of the present invention is a method for conditioning hair comprising applying to the hair a conditioning effective amount of a composition

10 comprising

(a) from 0.1 wt.% to 10 wt.% of a mixture of compounds of the formula (1)



15 wherein R¹ is alkyl containing 1 to 6 carbon atoms, or hydroxyalkyl containing 1 to 6 carbon atoms; R² is alkyl containing 1 to 6 carbon atoms, or benzyl; X⁻ is an anion; and R is selected from the group consisting of alkyl and alkylene groups containing 11 to 23 carbon atoms and up to 3 carbon-carbon double bonds, provided that said mixture contains compounds of formula (1) containing R groups which have at least 2 different chain lengths and containing R groups which have 0, 1 and 2 carbon-carbon double bonds; and

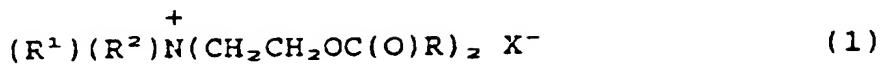
20 25 (b) a vehicle which imparts to said composition fluidity upon application thereof to the hair and which has a pH value compatible with said hair.

Another aspect of the present invention is a method for conditioning skin comprising applying to the skin a conditioning effective amount of a composition

30 comprising

-4-

1 (a) from 0.1 wt.% to 10 wt.% of a mixture of
compounds of the formula (1)

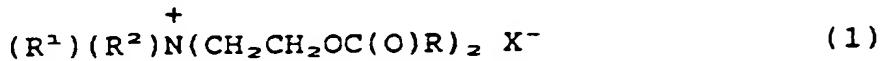


5 wherein R¹ is alkyl containing 1 to 6 carbon atoms, or
hydroxyalkyl containing 1 to 6 carbon atoms; R² is alkyl
containing 1 to 6 carbon atoms, or benzyl; X⁻ is an
anion; and R is selected from the group consisting of
10 alkyl and alkylene groups containing 11 to 23 carbon
atoms and up to 3 carbon-carbon double bonds, provided
that said mixture contains compounds of formula (1)
containing R groups which have at least 2 different
chain lengths and containing R groups which have 0, 1
and 2 carbon-carbon double bonds; and

15 (b) a vehicle which imparts to said
composition fluidity upon application thereof to the
skin and which has a pH value compatible with said skin.

Another aspect of the present invention is
compositions useful for conditioning hair, comprising

20 a) from 0.1 wt.% to 10 wt.% of a mixture of
compounds of the formula (1)



25 wherein R¹ is alkyl containing 1 to 6 carbon atoms, or
hydroxyalkyl containing 1 to 6 carbon atoms; R² is alkyl
containing 1 to 6 carbon atoms, or benzyl; X⁻ is an
anion; and R is selected from the group consisting of
alkyl and alkylene groups containing 11 to 23 carbon
atoms and up to 3 carbon-carbon double bonds, provided
that said mixture contains compounds of formula (1)
30 containing R groups which have at least 2 different

-5-

- 1 chain lengths and containing R groups which have 0, 1
and 2 carbon-carbon double bonds; and
 (b) a vehicle which imparts to said
composition fluidity upon application thereof to the
5 hair and which has a pH value compatible with said hair.

Yet another aspect of the present invention is compositions useful for conditioning skin, comprising

- (a) from 0.1 wt.% to 10 wt.% of a mixture of compounds of the formula (1)

$$10 \quad (R^1)(R^2)N(CH_2CH_2OC(O)R)_2 X^- \quad (1)$$

wherein R¹ is alkyl containing 1 to 6 carbon atoms, or hydroxyalkyl containing 1 to 6 carbon atoms; R² is alkyl containing 1 to 6 carbon atoms, or benzyl; X⁻ is an anion; and R is selected from the group consisting of alkyl and alkylene groups containing 11 to 23 carbon atoms and up to 3 carbon-carbon double bonds, provided that said mixture contains compounds of formula (1) containing R groups which have at least 2 different chain lengths and containing R groups which have 0, 1 and 2 carbon-carbon double bonds; and

DETAILED DESCRIPTION OF THE INVENTION

The compounds of formula (1) having any single chain length R and any given degree of saturation or unsaturation are known, individually, per se.

30 The desired mixture of compounds in accordance
with this invention having compounds of several
different chain lengths R and degrees of saturation and

-6-

1 unsaturation can be synthesized by a series of reactions
carried out under conditions familiar to those of
ordinary skill in this art. For instance, a methyl-
bis(2-hydroxyethyl) tertiary amine can be reacted with
5 an appropriate blend of fatty acids of the general
formula RC(O)OH as defined furthermore herein, the
reaction being carried out under esterifying conditions
with a sufficient amount of such fatty acids to provide
complete esterification of both hydroxyl groups on the
10 tertiary amine. Thereafter, the diesterified tertiary
amine is reacted with a quaternizing reagent of the
formula CH_3X , such as methylchloride or dimethylsulfate,
in order to provide a second methyl group onto the
nitrogen atom, thereby forming the desired quaternary
15 ammonium compound.

The substituents R^1 and R^2 defined hereinabove
are preferably both methyl, or both ethyl, or one is
methyl or ethyl and the other is benzyl or hydroxyalkyl,
preferably hydroxyethyl or hydroxymethyl.

20 In formula (1) as defined herein, the anion X^-
counterbalances the positive charge of the quaternary
ammonium compound. Thus, the quaternizing compound has
the formula CH_3X . The anion X is preferably any anion
forming the desired compound capable of quaternizing the
25 tertiary amines so as to form the desired dimethyl-
substituted quaternary ammonium compound. Preferred
examples of X^- include chloride, bromide and
methylsulfate.

Referring again to formula (1), the
30 substituent R is selected from the group consisting of
alkyl and alkylene groups containing 12 to 24 carbon

-7-

1 atoms and 0, 1, 2 or 3 carbon-carbon double bonds. It
has been determined that superior conditioning
properties are exhibited by compounds corresponding to
the above formula (1) provided that the compounds
5 corresponding to that formula (1) which are present in
the conditioning composition represent a mixture of
chain lengths of the substituent R and also represent a
mixture of saturated and mono-unsaturated and di-
unsaturated chains. It is recognized, of course, that
10 any one compound of formula (1) can have no more than
two particular R groups, and that within any one
molecule the R groups can be the same or different.
However, the superior conditioning properties that the
conditioning compositions of the present invention have
15 been found to possess are provided by including in the
compositions compounds corresponding to formula (1)
wherein compounds are present which exhibit R groups
containing at least five different chain lengths and
containing R groups which have no carbon-carbon double
20 bonds, R groups which have one carbon-carbon double
bond, and R groups which have two carbon-carbon double
bonds. Hair and skin conditioning compositions
containing mixtures of compounds of formula (1) have
been found to exhibit conditioning superior to that
25 exhibited by conditioning agents of formula (1) wherein
all the R groups are the same.

The requirement that the conditioning
compositions contain compounds of formula (1) exhibiting
a number of different chain lengths and degrees of
30 saturation can be readily met by reacting the precursor
bis(hydroxyl) tertiary amine with products containing a

-8-

1 mixture of fatty acids of varying chain lengths and
varying degrees of unsaturation. Such mixtures of acids
are known and are commercially available as, for
instance, tallow acids, rapeseed oil acids, palm oil
5 acids, palm stearine acids, and canola oil acids, which
are particularly preferred examples as used in the
present invention. The fatty acids present in each of
these naturally occurring products contain five or more
different chain lengths and contain acids having no
10 unsaturation, as well as acids which are mono-
unsaturated, di-unsaturated and tri-unsaturated. More
particularly, the distribution of fatty acids and their
chain lengths and number of double bonds are set forth
in the following table.

15 The following table describes tallow acids and
rapeseed oil acids, which are two preferred acid
mixtures useful in this invention. Each number
represents a percent by weight of the entire mixture of
acids and has a margin of \pm 0.2 wt.%.

20

25

30

35

-9-

1

	Fatty Acids	Carbon Atoms	Double Bonds	Tallow	Rapeseed Oil
5	Lauric	12	0	0.1	---
	Myristic	14	0	3.2	0.1
	Myristoleic	14	1	0.9	---
	Pentadecanoic	15	0	0.5	---
	Palmitic	16	0	24.3	3.8
10	Palmitoleic	16	1	3.7	0.3
	Margaric	17	0	1.5	---
	Margaroleic	17	1	0.8	---
	Stearic	18	0	18.6	1.2
	Oleic	18	1	42.6	18.5
15	Linoleic	18	2	2.6	14.5
	Linolenic	18	3	0.7	11.0
	Arachidonic	20	0	0.2	0.7
	Gadoleic	20	1	0.3	6.6
	Eicosadienoic	20	2	---	0.7
20	Behenic	22	0	---	0.5
	Erucic	22	1	---	41.1
	Lignoceric	24	0	---	1.0
Iodine Value Range				40-55	100-115

25

The compositions according to the present invention can be formulated with any cosmetically acceptable vehicle which is inert to the conditioning agent and to the hair or skin, as the case may be. By "cosmetically acceptable" is meant that the vehicle is

35

-10-

1 inert to the skin or hair and permits easy, even
application to the skin or hair of a thin film which
contains the reaction product. Such vehicles can
comprise any of a large variety of forms, including oil-
5 in-water emulsions, water-in-oil emulsions, anhydrous
compositions such as oil-based liquids, slurries,
powders or pastes, and aqueous solutions, slurries and
pastes. The conditioning compositions preferably
contain a total of from about 0.1 wt.% to about 10 wt.%
10 of the indicated mixture of compounds of the formula
(1).

Compositions according to this invention can
include water as a vehicle, usually with at least one
other cosmetically-acceptable vehicle.

15 Vehicles other than water that can be used in
compositions according to the invention can include
liquids or solids as emollients, solvents, humectants,
thickeners and powders. Examples of each of these types
of vehicles, which can be used singly or as mixtures of
20 one or more vehicles, are as follows:

Emollients, such as stearyl alcohol, glyceryl
ricinoleate, glyceryl stearate, propane-1,2-diol,
butane-1,3-diol, mink oil, cetyl alcohol,
stearamidopropyl dimethylamine, isopropyl isostearate,
25 stearic acid, isobutyl palmitate, isocetyl stearate,
oleyl alcohol, isopropyl laurate, hexyl laurate, decyl
oleate, octadecan-2-ol, isocetyl alcohol, eicosanyl
alcohol, behenyl alcohol, cetyl palmitate, silicone oils
such as dimethylpolysiloxane, dimethicone copolyols, di-
30 n-butyl sebacate, isopropyl myristate, isopropyl
palmitate, isopropyl stearate, butyl stearate,

-11-

1 polyethylene glycol, triethylene glycol, lanolin, cocoa butter, corn oil, cotton seed oil, tallow, lard, olive oil, palm kernel oil, rapeseed oil, safflower seed oil, soybean oil, sunflower seed oil, olive oil, sesame seed
5 oil, coconut oil, arachis oil, castor oil, acetylated lanolin alcohols, petrolatum, mineral oil, butyl myristate, isostearic acid, palmitic acid, isopropyl linoleate, lauryl lactate, myristyl lactate, decyl oleate, myristyl myristate;

10 Solvents such as ethyl alcohol, propylene glycol, water, isopropanol, castor oil, ethylene glycol monoethyl ether, diethylene glycol monobutyl ether, diethylene glycol monoethyl ether, dimethyl sulphoxide, dimethyl formamide, tetrahydrofuran;

15 Humectants, such as glycerin, sorbitol, sodium 2-pyrrolidone-5-carboxylate, soluble collagen, dibutyl phthalate, propylene glycol, gelatin;

Powders can include components such as chalk, talc, fullers earth, kaolin, starch, gums, colloidal
20 silicon dioxide, sodium polyacrylate, tetra alkyl and/or trialkyl aryl ammonium smectites, chemically modified magnesium aluminum silicate, organically modified montmorillonite clay, hydrated aluminum silicate, fumed silica, carboxyvinyl polymer, cellulosics such as
25 hydroxyethyl cellulose and sodium carboxymethyl cellulose, ethylene glycol monostearate, zinc or magnesium stearate, zinc oxide and magnesium oxide. These components may also be used as thickeners in fluid or semi-fluid compositions.

30 Examples of additional composition types are found in Encyclopedia of Chemical Technology, Vol. 7,

-12-

1 Pages 146-150 and 155-160 (John Wiley & Sons, 1979), the disclosure of which is hereby incorporated herein by reference.

Examples of other conventional adjuncts, some
5 of which can also function as vehicles, that may optionally be employed, include volatile and non-volatile silicones; silicone polymers; preservatives, such as para-hydroxy benzoate esters; humectants, such as butane-1,3-diol, glycerol, sorbitol, polyethylene
10 glycol; stabilizers, such as sodium chloride or ammonium chloride; buffer systems, such as lactic acid together with a base such as sodium hydroxide; oils and waxes, such as avocado oil, Evening Primrose oil, mineral oil, petrolatum, sunflower oil, beeswax, ozokerite wax,
15 paraffin wax, lanolin, lanolin alcohol; emollients; thickeners; activity enhancers; colorants; whiteners; fragrances; and bactericides.

When the desired conditioning composition is a solution, one can simply stir together the desired
20 amount of the mixture of compounds of formula (1) together with the solvent, such as water or, for instance, a lower alcohol containing 1-6 carbon atoms in which the mixture is soluble, or a mixture of water and such an alcoholic component. A useful embodiment is a
25 solution of 85% active and 15% ethanol. A preferred embodiment is 75% active and 25% propylene glycol.

When it is desired that the composition is in the form of an emulsion, for instance as a cream or lotion, the composition should also contain an
30 emulsifier component which is constituted of one or more emulsifiers chosen to provide the HLB (hydrophilic-

-13-

- 1 lipophilic balance) appropriate to whether the aqueous or oil phase is the continuous phase, and appropriate to the choice of the particular components present.
- 5 Suitable cosmetically acceptable emulsifiers abound and are well known to the cosmetic chemist. Examples include compounds having a long-chain alkyl or alkylene chain of 12 to 20 carbon atoms substituted with a chain of 4 to 20 ethoxy or propoxy units; and glycol or glycerol derivatives substituted with an alkyl or
- 10 alkylene chain of 12 to 24 carbon atoms. Further examples are found in Encyclopedia of Chemical Technology, Vol. 8, Pages 913-916 (John Wiley & Sons, 1979), which are hereby incorporated herein by reference.
- 15 The topical skin conditioner compositions of the invention can be formulated as a fluid, for example in a product such as a lotion, with or without an applicator such as a roll-ball applicator, or a container fitted with a pump to dispense the
- 20 composition, for example as a cream or mousse, or simply in a non-deformable bottle or squeeze container. Alternatively, the composition of the invention may be semi-solid, for example as a cream, lotion, gel, paste or ointment for use in conjunction with a suitable
- 25 applicator or simply in a tube or lidded jar. Hair and skin conditioner compositions are preferably flowable liquids (solutions, emulsions or dispersions) although they can be in the form of thickened gels, pastes and the like that can be rubbed into and onto the hair or
- 30 skin.

-14-

1 The conditioning compositions useful in the
present invention will preferably contain in addition
substances effective to adjust the pH of the composition
to values within desired ranges compatible with the
5 surface to which the conditioning agent will be applied.
Thus, for instance, it is preferred that the pH of a
hair conditioning composition be in the range of about
4.0 to about 5.5 in order to provide proper
compatibility with the hair shaft itself. It is
10 preferred that skin conditioning compositions have a pH
of about 3.5 to about 5.5 in order to provide proper
conditioning to the skin while avoiding irritation that
would ensue from pH values that are too low or too high.
Suitable agents for adjusting the pH to within these
15 desired limits without otherwise disturbing the desired
attributes of the conditioning compositions include
citric acid (to adjust the pH downwards) and small
amounts of sodium hydroxide (to adjust the pH upwards).

The conditioning compositions can also contain
20 additional adjuvants which enhance the conditioning
properties of the compositions and agents which provide
fluidity to the composition. As is familiar to those
having experience in this field, the conditioning
compositions are preferably flowable liquids which
25 retain sufficient viscosity that they do not immediately
run off of the surface to which they are applied.

Thus, it is preferred that the conditioning
compositions include one or more fatty alcohols, by
which is meant compositions of the formula R^1OH wherein
30 R^1 represents an alkyl or alkylene group, straight or

-15-

1 branched, containing 12-22 carbon atoms and 0, 1 or 2
carbon-carbon double bonds.

The formulation of the compositions is
straightforward and well within the skill of those
5 familiar with the manufacture of conditioning
compositions. The ingredients are stirred together in a
suitable mixing vessel until a homogeneous flowable
composition is formed. The composition is then metered
into appropriate containers, sealed and available for
10 shipment to the point of purchase.

The resulting conditioning compositions can be
used in the manner presently employed with conventional
hair conditioning compositions and skin conditioning
compositions. For use on the hair, it is adequate to
15 pour an amount generally ranging from about 1 to about 5
grams onto the hair, to work it into the hair
thoroughly, and then to rinse it from the hair. For
skin conditioning compositions, amounts generally used
are on the order of 0.5 to 2 fluid ounces which are
20 applied to the skin or applied to the hands and then
rubbed onto the skin with any excess amounts of
conditioner simply wiped off of the skin. It will be
recognized that the appropriate amount to use can
readily be ascertained as a function of the conditioning
25 effect imparted by the composition and as a function of
the volume of hair or area of skin that is desired to be
conditioned.

The present invention will be further
illustrated in the following examples, which are
30 included for purposes of illustration and are not
intended to be limiting.

-16-

1

EXAMPLE 1

This example compares compositions in accordance with the present invention with other formulations for properties as a hair conditioner.

5 The formulations that were tested were:

Formulation 1-1

	<u>Ingredient</u>	<u>Wt.%</u>
10	Quaternium-18 (dimethyldihydrogenated tallow ammonium chloride), 68% active in propylene glycol ("Varisoft 432 PPG," Witco Chemical Co.)	1.47
15	Cetyl Alcohol $(CH_3(CH_2)_{15}OH)$	2.0
15	Ceteareth-20 (having the formula $R(OCH_2CH_2)_nOH$ wherein R is a mixture of cetyl and stearyl and n has an average value of 20) Citric acid, as 25 wt.% solution in water	1.0
20	DI (deionized) Water	to pH 4.0-4.4 95.53

Formulation 1-2

	<u>Ingredient</u>	<u>Wt.%</u>
25	PPG-9 Dimethylmonium chloride (Methyl-diethyl-poly(propoxy)- ammonium chloride having an average of 9 propoxy units) 95% active in water ("Emcol CC-9," Witco Chemical Co.)	1.05
30	Cetyl Alcohol	2.0
30	Ceteareth-20	1.0
30	Citric acid, as 25 wt.% solution in water	to pH 4.0-4.4
	DI Water	95.95

-17-

1 Formulation 1-3

	<u>Ingredient</u>	<u>Wt.%</u>
5	PPG-40 Diethylmonium chloride (Methyl-diethyl-poly(propoxy)- ammonium chloride having an average of 40 propoxy units) ("Emcol CC-42," Witco Chemical Co.)	1.05
10	Cetyl Alcohol Ceteareth-20 Citric acid, as 25 wt.% solution in water	2.0 1.0 to pH 4.0-4.4
	DI Water	95.95

Formulation 1-4

	<u>Ingredient</u>	<u>Wt.%</u>
15	Steapyrium chloride (1-(2-hydroxyethyl) carbamoyl methyl pyridinium chloride stearate), 94% active ("Emcol E-607S," Witco Chemical Co.)	1.06
20	Cetyl Alcohol Ceteareth-20 DI Water Citric acid, as 25 wt.% solution in water	2.0 1.0 95.94 to pH 4.0-4.4

Formulation 1-5

	<u>Ingredient</u>	<u>Wt.%</u>
25	Lapyrium chloride (1-(2-hydroxyethyl) carbamoyl methyl pyridinium chloride laurate), 97.5% active ("Emcol E-607L," Witco Chemical Co.)	1.06
30	Cetyl Alcohol Ceteareth-20 DI Water Citric acid, as 25 wt.% solution in water	2.0 1.0 95.97 to pH 4.0-4.4

-18-

1 Formulation 1-6

	<u>Ingredient</u>	<u>Wt.%</u>
5	Mixture of compounds of formula (1), derived from soft (partially hydrogenated) tallow acids, 82% actives, $X = Cl$	1.22
10	Cetyl Alcohol	2.0
	Ceteareth-20	1.0
	DI Water	95.78
	Citric acid, as 25 wt.% solution in water	to pH 4.0-4.4

Formulation 1-7

	<u>Ingredient</u>	<u>Wt.%</u>
15	Mixture of compounds of formula (1), derived from hydrogenated tallow acids, 82% active, $X = Cl$	1.22
20	Cetyl Alcohol	2.0
	Ceteareth-20	1.0
	DI Water	95.78
	Citric acid, as 25 wt.% solution in water	to pH 4.0-4.4

Each formulation was prepared as follows: the water, and separately the ingredients other than water or citric acid, were measured into separate beakers.

25 Each beaker was heated over a steam bath until the contents were at 75-80°C. The beakers were then removed from the heat, the contents were combined and stirred until cool, and citric acid as necessary was added.

A hair swatch evaluation test was then performed to assess the performance of each formulation as a hair conditioner. Hair swatches were prepared and tested as follows:

-19-

1 Hair for the tests was certified virgin European brown hair. The hair samples were banded and glued in 5 gram tresses.

Procedure:

- 5 1. Wet hair tress with warm tap water and apply 3 cc of a 5 wt.% solution of sodium lauryl sulfate in deionized water.
2. Wash hair for 2 minutes and rinse for 1 minute under running tap water at 40°C.
- 10 3. Squeeze excess water from hair and place tress in large weighing dish.
4. Weigh 0.5 gram of a 1% active conditioner onto the hair tress.
- 15 5. Massage conditioner evenly through the hair for 2 minutes and rinse for 1 minute under running tap water at 40°C.
6. Squeeze out excess water and blot dry between layers of paper towels.
- 20 7. Comb hair and evaluate for wet comb and wet detangle.
8. Roll hair onto a 1-inch plastic roller and hang to dry overnight.
9. Remove roller and evaluate for dry characteristics including dry comb, manageability, dry detangle, bounce/body, curl, and shine.
- 25 10. Report results as a number (5 = best) and/or use descriptive words.

These results indicate that hair conditioning compositions in accordance with the present invention exhibit superior conditioning.

-20-

1 The results are set forth in the following
Table 1:

5 Table 1

	<u>Conditioner Formulation</u>	<u>1-1</u>	<u>1-2</u>	<u>1-3</u>	<u>1-4</u>	<u>1-5</u>	<u>1-6</u>	<u>1-7</u>
10	Feel on Hair	3.0	3.0	2.5	4.0	4.5	5.0	5.0
	Rinsability	3.5	3.0	3.5	4.0	4.5	4.5	4.5
	Wet Comb	3.5	3.0	3.0	4.0	4.5	4.5	4.5
	Detangle	3.0	3.0	2.5	3.5	4.5	4.5	4.0
15	Dry Comb	3.0	3.0	2.5	4.0	3.5	4.0	4.0
	Detangle	3.5	2.5	2.0	4.5	3.5	4.0	3.5
	Antistatic	2.5	2.5	2.0	3.5	3.0	3.5	3.5
20	Bounce/Body	3.5	3.0	2.5	3.0	3.0	3.5	3.5
	Manageability	3.0	3.0	2.5	3.5	3.0	3.5	3.5
	Shine	3.0	3.0	2.0	3.0	3.0	3.0	3.0
25	Total (Average)	3.15	2.9	2.5	3.7	3.7	4.0	3.9

These results indicate that hair conditioning compositions in accordance with the present invention 30 exhibit superior conditioning compound to compositions based on other conditioning agents.

-21-

1

EXAMPLE 2

This example compares compositions in accordance with the present invention with compositions based on agents of a single chain length R.

5

The formulations that were tested were:

Formulation 2-1

	<u>Ingredient</u>	<u>Wt.%</u>
10	A compound corresponding to formula (1) except that both R groups were C ₁₃ alkyl, X = Cl	1.0
	Cetyl Alcohol	2.0
	Ceteareth-20	1.0
	DI Water	96.0
15	Citric acid, as 25 wt.% solution in water	to pH 4.0-4.4

Formulation 2-2

	<u>Ingredient</u>	<u>Wt.%</u>
20	A compound corresponding to formula (1) except that both R groups were C ₁₅ alkyl, X = Cl	1.0
	Cetyl Alcohol	2.0
	Ceteareth-20	1.0
	DI Water	96.0
25	Citric acid, as 25 wt.% solution in water	to pH 4.0-4.4

30

35

-22-

1 Formulation 2-3

	<u>Ingredient</u>	<u>Wt.%</u>
5	A compound corresponding to formula (1) except that both R groups were C ₁₂ alkyl, X = Cl	1.0
	Cetyl Alcohol	2.0
	Ceteareth-20	1.0
	DI Water	96.0
	Citric acid, as 25 wt.% solution in water	to pH 4.0-4.4

10

Formulation 2-4

	<u>Ingredient</u>	<u>Wt.%</u>
15	Conditioning agent of formula (1) derived from hydrogenated tallow acids, X = CH ₃ SO ₄	1.0
	Cetyl Alcohol	2.0
	Ceteareth-20	1.0
	DI Water	96.0
	Citric acid, as 25 wt.% solution in water	to pH 4.0-4.4

20

Formulation 2-5

	<u>Ingredient</u>	<u>Wt.%</u>
25	Conditioning agent as in Formulation 2-4 except that all R groups were C ₁₂ alkyl	1.0
	Cetyl Alcohol	2.0
	Ceteareth-20	1.0
	DI Water	96.0
	Citric acid, as 25 wt.% solution in water	to pH 4.0-4.4

30

35

-23-

1 Formulation 2-6

	<u>Ingredient</u>	<u>Wt.%</u>
5	Conditioning agent of formula (1) derived from rapeseed oil acids, X = Cl, (71.3% actives)	1.15
	Cetyl Alcohol	2.0
	Ceteareth-20	1.0
	DI Water	95.85
10	Citric acid, as 25 wt.% solution in water	to pH 4.0-4.4

10

Each formulation was prepared by combining the first listed product and the water in one container, combining the other ingredients in a separate container, heating each container over a steam bath until the 15 contents were at 75-80°C, removing the heat, combining the contents of the two containers, and stirring the product until cool.

15

Each formulation was then tested on hair following the procedure described in Example 1. The 20 results are set forth in Table 2:

25

30

35

-24-

1

Table 2

	<u>Conditioner Formulation</u>	<u>1-1</u>	<u>1-6</u>	<u>1-7</u>	<u>2-1</u>	<u>2-2</u>	<u>2-3</u>	<u>2-4</u>	<u>2-5</u>	<u>2-6</u>
5	Feel on Hair	3.0	5.0	5.0	2.7	4.9	4.9	4.9	2.6	5.0
	Rinsability	3.5	4.5	4.5	3.5	4.5	4.5	4.5	3.3	4.5
	Wet Comb	3.2	4.5	4.5	2.9	4.6	4.5	4.5	2.5	4.6
	Detangle	3.0	4.6	4.4	2.3	4.0	4.2	4.5	2.1	4.6
	Dry Comb	3.3	4.0	4.0	2.7	4.0	4.0	3.9	2.0	4.2
	Detangle	3.5	4.0	3.7	3.0	4.5	4.5	4.0	2.5	4.3
	Antistatic	2.5	3.5	3.5	2.3	3.0	3.5	3.0	2.3	3.0
	Bounce/Body	3.5	3.5	3.5	3.0	3.5	3.5	3.2	2.9	3.2
	Manageability	3.0	3.5	3.5	3.0	3.5	3.5	3.2	2.9	3.2
20	Shine	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
	Total(Average)	3.15	4.01	3.96	2.84	3.95	4.01	2.86	2.61	3.96

25 These data show that conditioning agents based
on a combination of compounds having a range of R chain
lengths have superior performance even though they
include compounds which used singly exhibit poorer
conditioning and would thus be expected to detract from
30 the performance of the combination.

-25-

1

EXAMPLE 3

This example describes the preparation of conditioner compositions of this invention.

5 Formulation 3-1: Hair Conditioner

	<u>Ingredient</u>	<u>Wt.%</u>
	Glyceryl Stearate	1.0
	Cetyl Alcohol	1.5
	Conditioning agent of formula 10 (1) derived from rapeseed oil acids, X = Cl (71.3% actives)	1.4
	DI Water	95.0
	Hydroxyethylcellulose - "Natrosol 250 HHR CS" (Aqualon)	1.0
	Dimethicone Copolyol - Dow Corning 193	0.1
15	Citric Acid (25% aqueous)	to pH 4.5-5.5
	Perfume	q.s
	Preservative	q.s
		<u>100%</u>

Procedure:

- 20 Weigh water into a container. Sprinkle in Natrosol with mixing until there is an even distribution. Weigh glyceryl stearate, cetyl alcohol, and rapeseed conditioning agent into a separate container. Heat the contents of each beaker over a steam bath to 70-75°C. Remove water cellulose mixture from bath, attach to agitator, then add in the contents of the other container to the water with mixing. The combination temperature was recorded at 70°C. Allow to cool. At 50°C add premeasured dimethicone copolyol.
- 25 30 After 24 hours the pH was adjusted with 25% citric acid.

-26-

1 Viscosity: Brookfield Viscometer DV2
Spindle No. 5 at 10 rpm.
8,000 cps.

The product was a creamy, thick, white liquid
5 at room temperature and retained this condition, without
breaking, upon heating to 48°C and after 3 freeze/thaw
cycles. As a hair conditioner it provides excellent
feel and detangling benefits.

10 Formulation 3-2: Hair Conditioner

	<u>Ingredient</u>	<u>Wt.%</u>
	DI Water	90.7
	Cetyl Alcohol	3.0
	Stearyl Alcohol	0.5
15	Conditioning agent of formula (1) derived from rapeseed oil acids, X = Cl (71.3% actives)	2.8
	Ceteareth-20	0.4
	Stearamidopropyl Dimethylamine	0.3
	DI Water	2.0
20	Hydrolyzed Protein - "Crotein SPC" (Croda)	0.3
	Citric Acid (25% aqueous)	to pH 4.5-5.5
	Perfume	q.s
	Preservative	q.s
		100%

25 Observations & Data:

The water was weighed into a container. The
other ingredients other than water and citric acid were
weighed into a separate container. The contents of each
container were heated over a steam bath to 70-75°C. The
water was removed from the steam bath and attached to a
30 mixer, and the second container contents were added with
agitation. The mixture was allowed to cool with mixing.

-27-

1 At 30°C premixed water and hydrolyzed protein were added. After set-up the pH was adjusted with citric acid.

5 Viscosity: Brookfield DV2 Viscometer.

Spindle No. 5 at 10 rpm.

2,520 cps.

The product was a thin, creamy, white liquid

and retained this condition, without breaking, upon

10 heating at 48°C and after 3 freeze/thaw cycles. It is a deep conditioning hair conditioner with exceptional afterfeel.

Formulation 3-3: Skin Lotion

	<u>Amt. (gr.)</u>
Glyceryl Stearate	4.0
"Protol" (Mineral Oil) (Witco Corp.)	2.0
Cetyl Alcohol	1.0
PEG-8 Stearate	1.0
Conditioning agent of formula 20 (1) derived from rapeseed oil acids, X = Cl, 71.3% actives	1.3
Dow Corning fluid 200 250 CS (Dow Chemical)	0.4
DI Water	86.3
Glycerine	4.0
Lactic Acid	pH 4.5 - 5.0
pH = 3.9	

25 Viscosity: Brookfield DV2 Viscometer.

Spindle No. 4 at 20 rpm.

78,000 cps.

The product appeared to be a water-in-oil

30 emulsion and imparted a silky feeling to the skin.

-28-

1 Formulation 3-4: Skin Lotion

Amt. (gr.)

PPG-3 Myristyl ether	6.0
Glyceryl stearate	3.5
Conditioning agent of formula 5 (1) derived from rapeseed oil acids, X = Cl	1.3
PEG-8 Stearate	1.0
Cetyl Alcohol	0.5
Petrolatum	1.0
Glycerine	4.0
Lactic Acid	0.05
10 DI Water	82.65

Viscosity: Brookfield DV2 Viscometer.

Spindle No. 4 at 20 rpm.

3,200 cps.

15

This product is an oil-in-water emulsion with
good after-dry feel.

20

25

30

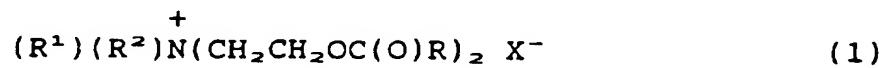
35

-29-

1 WHAT IS CLAIMED IS:

1. A method for conditioning hair comprising applying to the hair a conditioning effective amount of a composition comprising

5 (a) from 0.1 wt.% to 10 wt.% of a mixture of compounds of the formula (1)



wherein R¹ is alkyl containing 1 to 6 carbon atoms, or
10 hydroxyalkyl containing 1 to 6 carbon atoms; R² is alkyl containing 1 to 6 carbon atoms, or benzyl; X⁻ is an anion; and R is selected from the group consisting of alkyl and alkylene groups containing 11 to 23 carbon atoms and up to 3 carbon-carbon double bonds, provided
15 that said mixture contains compounds of formula (1) containing R groups which have at least 2 different chain lengths and containing R groups which have 0, 1 and 2 carbon-carbon double bonds; and

(b) a cosmetically acceptable vehicle which
20 imparts to said composition fluidity upon application thereof to the hair and which has a pH value compatible with said hair.

2. A method according to Claim 1 wherein the pH value of said composition is about 3.5 to about 5.5.

25 3. A method according to Claim 1 wherein said composition is a solution.

4. A method according to Claim 1 wherein said composition is a water-in-oil emulsion.

30 5. A method according to Claim 1 wherein said composition is an oil-in-water emulsion.

-30-

1 6. A method according to Claim 1 wherein the
structures of the R groups and the amounts thereof are
those of tallow.

5 7. A method according to Claim 1 wherein the
structures of the R groups and the amounts thereof are
those of palm stearine.

 8. A method according to Claim 1 wherein the
structures of the R groups and the amounts thereof are
those of palm oil.

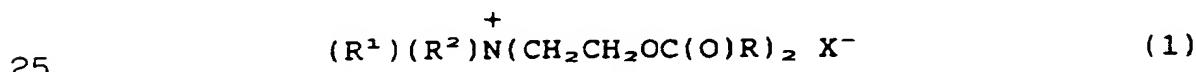
10 9. A method according to Claim 1 wherein the
structures of the R groups and the amounts thereof are
those of canola oil.

15 10. A method according to Claim 1 wherein the
structures of the R groups and the amounts thereof are
those of rapeseed oil.

 11. A method according to Claim 1 wherein X⁻
is selected from the group consisting of chloride,
bromide, methylsulfate and ethylsulfate.

20 12. A method for conditioning skin comprising
applying to the skin a conditioning effective amount of
a composition comprising

 (a) from 0.1 wt.% to 10 wt.% of a mixture of
compounds of the formula (1)



25 wherein R¹ is alkyl containing 1 to 6 carbon atoms, or
hydroxyalkyl containing 1 to 6 carbon atoms; R² is alkyl
containing 1 to 6 carbon atoms, or benzyl; X⁻ is an
anion; and R is selected from the group consisting of
30 alkyl and alkylene groups containing 11 to 23 carbon
atoms and up to 3 carbon-carbon double bonds, provided
that said mixture contains compounds of formula (1)

-31-

1 containing R groups which have at least 2 different chain lengths and containing R groups which have 0, 1 and 2 carbon-carbon double bonds; and

(b) a cosmetically acceptable vehicle which
5 imparts to said composition fluidity upon application thereof to the skin and which has a pH value compatible with said skin.

13. A method according to Claim 12 wherein
the pH value of said composition is about 4.0 to about
10 5.5.

14. A method according to Claim 12 wherein
said composition is a solution.

15. A method according to Claim 12 wherein
said composition is a water-in-oil emulsion.

16. A method according to Claim 12 wherein
said composition is an oil-in-water emulsion.

17. A method according to Claim 12 wherein
the structures of the R groups and the amounts thereof
are those of tallow.

18. A method according to Claim 12 wherein
the structures of the R groups and the amounts thereof
are those of rapeseed oil.

19. A method according to Claim 12 wherein
the structures of the R groups and the amounts thereof
25 are those of palm stearine.

20. A method according to Claim 12 wherein
the structures of the R groups and the amounts thereof
are those of palm oil.

21. A method according to Claim 12 wherein
30 the structures of the R groups and the amounts thereof
are those of canola oil.

-32-

1 22. A method according to Claim 12 wherein X⁻
is selected from the group consisting of chloride,
bromide, methylsulfate and ethylsulfate.

5

10

15

20

25

30

35

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/09960

A. CLASSIFICATION OF SUBJECT MATTERIPC(6) :A61K 7/06, A61K 47/00
US CL :424/070; 514/788, 514/847

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 424/070, 514/847

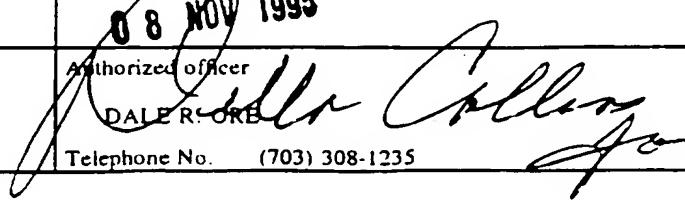
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4,978,526 (GESSLIN ET AL) 18 December 1990, column 2, lines 1-37.	12-22
X	WO, A, 91/17975 (BEROL NOBEL AB) 28 NOVEMBER 1991, see whole document, especially pages 8 and 9.	1-11
X	Ash et al, "A FORMULARY OF COSMETIC PREPARATIONS", published 27 July 1981 by Chemical Publishing Co. (New York), pages 119-129.	1-11

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
17 OCTOBER 1995	08 NOV 1995

Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer DALE R. ORB 
Faxsimile No. (703) 305-3592	Telephone No. (703) 308-1235

Form PCT/ISA/210 (second sheet)(July 1992)*

